

## Rotating Ring Disk Electrode Studies of Solvent Reduction and Oxidation

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### Introduction

The typical operational potential of a lithium battery is between 0 and 5 V, the range of which is beyond the thermodynamic range of most organic solvents it employed. Solvents, therefore, can be reduced and/or oxidized at the negative and positive electrodes during the battery charging process. The mechanism of electrolyte decomposition is a complicated process and no clear understanding has been reached despite a large research effort that was put in. Utilizing the tools of computational chemistry in combination with experimental techniques such as Cyclic Voltammetry (CV), IR, AFM and XPS, we were able to shed some light on the solvent reduction and oxidation mechanisms<sup>1,2</sup>. Rotating ring disk electrode is another useful technique in investigation of the initial reaction product of organic solvents<sup>3</sup>. A common supporting electrolyte based on THF is adopted to ensure a controlled environment for all solvents studies. THF is chosen due to its stability against reduction above the lithium metal potential.

### Experimental Section

Tetrahydrofuran (THF) (Aldrich, 99.9+%, HPLC grade), ethylene carbonate (EC) (Grant Chemical, less than 20 ppm H<sub>2</sub>O), LiClO<sub>4</sub> (EM industries), DMC (Grant Chemical, less than 20 ppm H<sub>2</sub>O), DEC (Grant Chemical, less than 20 ppm H<sub>2</sub>O), PC (Grant Chemical, less than 20 ppm H<sub>2</sub>O), and VC (Aldrich, 97%) were used as received without further purification. A single compartment polypropylene cell was used for the electrochemical experiments. Lithium metal was used for both counter and reference electrodes. The target solvent species was dissolved in a THF/0.1M LiClO<sub>4</sub> supporting electrolyte to a concentration typically of 2 vol % (3 wt % in the case of EC). The RRDE system (Pine Instruments) consists of a 6 mm diameter glassy carbon disk electrode and a Pt ring electrode (1 mm width) with a gap 0.5 mm between them. The current collection efficiency is 0.2.

### Results and Discussions

Figure 1 shows both of the disk and ring current profile when the disk electrode was scanned from 2 to 0.5 V, holding the ring electrode at 3.5 V in a 3% EC/THF – LiClO<sub>4</sub> electrolyte. The speed of rotation is 2000 rpm. The ring anodic current indicates that some soluble species from the EC reduction diffuses to the ring and is re-oxidized. The ring current becomes noticeable at potentials above 1 V (disk potential) and reaches maximum when disk potential drops to 0.5 V. The oxidation current collected at the ring is approx. 5% of the reduction current put in at the disk. In some other experiments the disk potential was held at 0.5 V and the ring potential was scanned from 3.5 to 2.5 V. The results demonstrate that the reduced species are only re-oxidized above 3 V, consistent with Endo's report<sup>3</sup>. The large potential difference between the reduction and re-oxidation, C.A. 2 V, suggests that solvent decomposition occurs during the reduction process, i.e the species being oxidized are fragments from the reduction reaction. Similar experiments were conducted for PC, DEC,

DMC and VC solvents. Solvent oxidation reaction was also studied.

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### References

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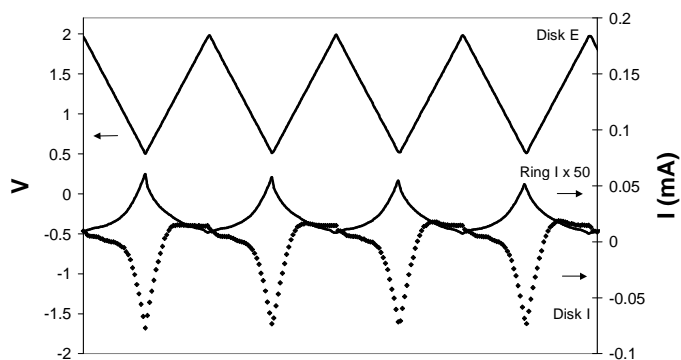


Figure 1